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1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE		3. DATES COVERED (From - To)	
		Technical Paper			
4. TITLE AND SUBTITLE				5a. CONTRACT NUMBER	F04611-99-C-0025
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	DARP
				5e. TASK NUMBER	A205
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)				8. PERFORMING ORGANIZATION REPORT	
ERC					
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				11. SPONSOR/MONITOR'S NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT					
Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
20021023 095					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
			A		Leilani Richardson
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER <i>(include area code)</i> (661) 275-5015
Unclassified	Unclassified	Unclassified			

Standard Form 298 (Rev. 8-98)  
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*1 item enclosed*

FILE

MEMORANDUM FOR PRS (In-House/Contractor Publication)

25 Sept 2002

FROM: PROI (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2002-224**  
Karl Christe (ERC) et al., "Tritylsulfinylamine: A New Member in the Family of Sulfinylamines"

55194

Solid State Sciences

Dr. C = 55881  
Deadline: 24 Oct 2002

(Statement A)

# **Tritylsulfinylamine: A New Member in the Family of Sulfinylamines**

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*Dedicated to Prof. Neil Bartlett on the occasion of his 70<sup>th</sup> birthday.*

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## **Abstract**

Triphenylmethyl N-sulfinylamine (trityl-NSO) was prepared from the reaction of trityl amine and SOCl<sub>2</sub>. Trityl-NSO was characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>14</sup>N NMR spectroscopy in

$\text{CH}_2\text{Cl}_2$  solution and by Raman and infrared spectroscopy in the solid state. Crystals of trityl-NSO were grown from n-heptane and characterized by single crystal X-ray diffraction ( $P\bar{1}$ ,  $a = 8.9642(9)$  Å,  $b = 9.2135(9)$  Å,  $c = 11.0645(11)$  Å,  $\alpha = 93.578(2)^\circ$ ,  $\beta = 101.098(2)^\circ$ ,  $\gamma = 118.142^\circ$ ,  $Z = 2$ , and  $R_{\text{int}} = 0.0332$  at 223 K). Trityl-NSO represents the first alkyl  $N$ -sulfinylamine that has been fully structurally characterized.

**Keywords:** *Triphenylmethylsulfinylamine; Vibrational spectroscopy; NMR spectroscopy, Crystal structure*

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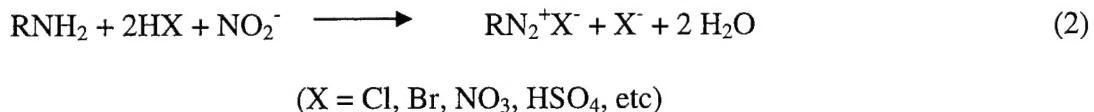
## 1. Introduction

There has been much recent interest in polynitrogen chemistry [1-9]. The successful synthesis of the  $\text{N}_5^+$  cation [10, 11] and the recent experimental detection of the  $\text{N}_5^-$  [12] anion by cleavage of *p*-hydroxyphenylpentazole prompted us to search for methods to prepare  $\text{N}_5^-$  salts in bulk. Since alkylpentazoles might be cleaved more readily than arylpentazoles, and diazonium salts are the precursors required for the preparation of pentazoles [13] (eq 1),

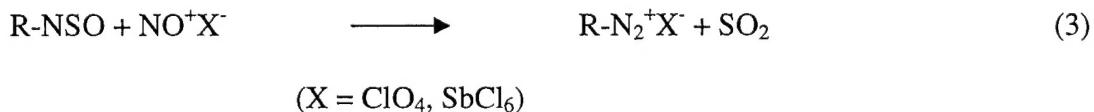


we became interested in the preparation of new alkyldiazonium salts. One of our targets in this area was the triphenylmethyldiazonium cation because of the exceptional stability of the triphenylmethyl (trityl) cation which would be formed as a by-product in the cleavage reaction of the C-N bond of the corresponding pentazole. Since the triphenylmethyldiazonium cation is unknown, methods for its synthesis were explored.

The synthesis of diazonium salts usually involves the reaction of nitrite with aryl amines in aqueous acids (eq 2).



However, this method cannot be used for trityl amine because the highly electrophilic carbon center of the methyl group is readily attacked by HX. Therefore, alternate methods were sought for the preparation of trityl-N<sub>2</sub><sup>+</sup>. One way to prepare diazonium salt under anhydrous, acid-free conditions employs the reaction of R-NSO with NO<sup>+</sup> [14] (eq. 3).



While more than 600 *N*-sulfinylamine compounds are known, trityl-NSO has not been reported. In the present paper, we report the preparation and full characterization of trityl-NSO.

## 2. Experimental Section

### 2.1. Materials and Apparatus

Reactions were carried out in Pyrex glass vessels closed by grease-free Kontes glass-Teflon valves. Volatile materials were handled on a Pyrex glass vacuum line equipped with the

same valves. Nonvolatile solids were handled in the dry argon atmosphere of a glove box. Infrared spectra were recorded on a Midac, M Series, FT-IR spectrometer using KBr pellets. The pellets were prepared inside the dry box using an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Bruker Equinox 55 FT-RA spectrometer using a Nd-Yag laser at 1064 nm and Pyrex melting point capillaries as sample containers. Nuclear magnetic resonance spectra were recorded unlocked on a Bruker AMX 500 NMR spectrometer at room temperature. The  $^1\text{H}$ ,  $^{13}\text{C}$  ( $^{14}\text{N}$ ) NMR spectra were referenced to external samples of neat TMS (neat nitromethane).

The starting materials,  $(\text{C}_6\text{H}_5)_3\text{CCl}$  (Aldrich),  $\text{NH}_3$  (Aldrich, anhydrous, 99.99%),  $\text{SOCl}_2$  (Aldrich),  $\text{Et}_3\text{N}$  (Aldrich), were used without further purification. Tritylamine,  $(\text{C}_6\text{H}_5)_3\text{CNH}_2$ , was prepared by literature methods [15]. The  $\text{CH}_2\text{Cl}_2$  (Mallinckrodt) and n-heptane (Aldrich, anhydrous 99%) were dried over molecular sieves.

## 2.2. Preparation of $(\text{C}_6\text{H}_5)_3\text{CNSO}$

In a typical experiment, a 15 mm diameter H-shaped Pyrex glass vessel with a frit, equipped with two concentric grease-free Teflon valves (Kontes) was loaded inside the glove box with  $(\text{C}_6\text{H}_5)_3\text{CNH}_2$  (1.989 mmol). Approximately 3 mL of  $\text{CH}_2\text{Cl}_2$  was condensed onto the solid at  $-196^\circ\text{C}$ , which dissolved completely upon warming to room temperature. At  $-196^\circ\text{C}$ , 0.403g (3.98 mmol)  $\text{NEt}_3$  was distilled onto the frozen  $\text{CH}_2\text{Cl}_2$  solution and allowed to warm to room temperature yielding a clear colorless solution. A stoichiometric amount of  $\text{SOCl}_2$  (1.98 mmol) was added in three increments followed by stirring for ca. 1 h. After the first addition, white  $\text{HNEt}_3^+\text{Cl}^-$  started to precipitate. The solution was stirred for further 18 h at room temperature resulting in a deep brown suspension. Removal of all volatile material under vacuum

was followed by repeated (20 times) extractions of the solid with a few mL n-heptane. Each time the n-heptane solution had been filtered through the frit, the n-heptane solvent was condensed back onto the solid at -196 °C in a static vacuum. The filtrate residue consisted of pale brown, solid  $(C_6H_5)_3CNSO$  (0.5288g , 1.732mmol, 87% yield).

### *2.3. Crystal Growth of $(C_6H_5)_3CNSO$*

Inside the dry box, 0.011g of  $(C_6H_5)_3CNSO$  (0.036 mmol) was loaded into a Pyrex glass vessel closed by a grease-free Teflon valve. n-Heptane (0.75 mL) was distilled onto the solid and most of it dissolved upon warming to room temperature. The solution was placed in an ethanol bath at -20 °C resulting in crystal growth. The n-heptane was slowly removed between -20 and -10 °C in a dynamic vacuum, resulting in further crystal growth.

### *2.4. Crystal Structure Determination of $(C_6H_5)_3CNSO$*

The single crystal x-ray diffraction data of  $Ph_3CNSO$  were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD (charge coupled device) detector with the  $\chi$ -axis fixed at 54.74° and using MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) from a fine-focus tube. This diffractometer was equipped with an LT-3 apparatus for low temperature data collection using controlled liquid nitrogen boil off. A few reasonably well-formed single crystals were selected in a glove-box, equipped with a CCD camera mounted microscope. The crystals were coated with epoxy grease and then mounted on a magnetic goniometer head. Cell constants were determined from 90 ten-second frames. A complete hemisphere of data was scanned on omega (0.3°) with a run time of thirty-second per frame at a detector resolution of 512 x 512 pixels using the SMART software [16]. A total of 1271 frames were collected in three sets and a final set of 50

frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed on a PC, running on Windows NT software, by using the SAINT software [17] to give the hkl file corrected for Lp/decay. The absorption correction was performed using the SADABS [18] program. The structure was solved by the direct method using the SHELX-90 program and refined by the least squares method on  $F^2$ , SHELXL-97 incorporated in SHELXTL Suite 5.10 for Windows NT [19]. All atoms were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The hydrogen atoms were located from difference electron density maps and refined in an isotropic manner.

### 3. Results and Discussion

#### 3.1. Synthesis and spectroscopic characterization of $(C_6H_5)_3CNSO$

Trityl-NSO was prepared following the method of Michaelis [20] which is based on the reaction of RNH<sub>2</sub> with SOCl<sub>2</sub>. The product was isolated in 87% yield by repeated extractions with n-heptane, yielding a pale brown solid with a melting point of 89 to 89.5 °C. Its purity was ascertained by IR, Raman and NMR spectroscopy. The IR and Raman spectra of trityl-NSO are shown in Fig. 1, and the vibrational frequencies are listed in Table 1 together with assignments for selected vibrations. Since the trityl skeleton gives rise to a complex vibrational spectrum, Raman spectra of a series of trityl compounds were recorded (Table 1), leading to the unambiguous identification of the vibrational frequencies associated with the NSO group. A thorough study of N-sulfinyl-benzamine [21] showed that the N=S and the S=O stretching vibrations are strongly coupled and that the NSO group gives rise to an out-of-phase and an in-

phase stretching mode. In trityl-NSO, the  $\nu_{as}$ (NSO) and the  $\nu_s$ (NSO) vibrations are assigned to  $1294\text{ cm}^{-1}$  and  $1123\text{ cm}^{-1}$ , respectively. In addition, the deformation mode,  $\delta$ (NSO), could be assigned to the band at  $585\text{ cm}^{-1}$ .

The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{14}\text{N}$  NMR spectroscopic data are listed in Table 2. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts lie in the region expected for the triphenylmethyl group. The broad  $^{14}\text{N}$  resonance for N-sulfinylamines at  $-39\text{ ppm}$  ( $\Delta\nu_{1/2} = 700\text{ Hz}$ ) is in the range observed for organic sulfinylamines [22].

### 3.2. Crystal Structure of $(\text{C}_6\text{H}_5)_3\text{CNSO}$

Details of the crystal data for  $(\text{C}_6\text{H}_5)_3\text{CNSO}$  are provided in Table 3; the atomic coordinates and equivalent isotropic displacement parameters are listed in Table 4; and the observed bond lengths, angles, and contacts are listed in Table 5.

The tritylsulfinylamine crystallizes in the triclinic space group  $P\bar{1}$  and is the first structurally characterized aliphatic derivative containing an NSO group. Three phenyl groups bonded to the tertiary carbon are oriented in a propeller-like fashion as shown in Fig. 2. The NSO group is oriented closest to the C(2)-C(7) phenyl ring as seen from the S(1)-N(1)-C(1)-C(2) torsion angle of  $40.3(2)^\circ$ . For the other two phenyl rings, this torsion angle increases to  $82.1(2)^\circ$  and  $159.5(1)^\circ$  for S(1)-N(1)-C(1)-C(8) and S(1)-N(1)-C(1)-C(14), respectively. The N=S=O angle of  $122.61(8)^\circ$  is also the largest known angle out of all the reported structures containing an uncoordinated terminal NSO group [23-30]. The next closest NSO angle reported is  $121.87^\circ$  for 2,4,6-tri-t-butyl-N-sulfinylaniline [25]. The CNSO fragment possesses the expected *syn* configuration [31] with respect to the SN double bond. The crystal lattice does not show any short-range intermolecular contacts, the closest one being H(12) $\cdots$ O(1)( $-1+x, -1+y, z$ )  $2.75(3)\text{ \AA}$ .

However, there are intramolecular hydrogen bonds [32] resulting from S(1), O(1) and N(1) i.e., S(1)…H(15) = 2.93(2), S(1)…H(3) = 3.00(2) Å, O(1)…H(15) = 2.57(2) Å and N(1)…H(13) = 2.35(2) Å. The NSO groups show dimer formation via the S(1)…O(1) (-x, 1-y, 1-z) contacts at 3.299(2) Å (Fig. 2) which is roughly equal to the sum of the van der Waal radii for sulfur (1.8) and oxygen (1.52 Å).

## Conclusion

While more than 600 *N*-sulfinylamines are known, triphenylmethyl *N*-sulfinylamine represents only the 13<sup>th</sup> example of an organic sulfinylamine and the first example of an alkyl *N*-sulfinylamine that has been fully structurally characterized by single crystal X-ray diffraction. The N=S=O angle of 122.61(8)<sup>o</sup> is the largest known angle out of all the reported structures containing an uncoordinated terminal NSO group. In spite of the complexity of the vibrational spectra of trityl-NSO, the vibrational frequencies associated with the NSO group could be assigned.

## Acknowledgements

The authors thank the National Science Foundation, the Defense Advanced Research Projects Agency, and the Air Force Office of Scientific Research for financial support. M. G. thanks the Natural Sciences and Engineering Research Council of Canada for a postdoctoral fellowship, and R. H., the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship.

## **Supplementary material**

Tables of structure determination summary, atomic coordinates, bond lengths and angles and anisotropic displacement parameters of  $(C_6H_5)_3CNSO$  in CIF format has been sent to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1 EZ, UK as supplementary material No. SUP NB1-22 (28 pages) and can be obtained by contacting the CCDC (quoting the article details and the corresponding SUP number).

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**Table 1**  
**Vibrational Spectra of  $(C_6H_5)_3CNSO$  Compared to the Raman Spectra of Related Trityl Compounds.<sup>a</sup>**

$(C_6H_5)_3CNH_2$	$(C_6H_5)_3CCl$	$(C_6H_5)_3CN_3$	$(C_6H_5)_3COH$	$(C_6H_5)_3CNF_2$	$(C_6H_5)_3CNSO$ Raman	IR
3367(2)						$\nu(NH_2)$
3301(4)						
3192(2)	3193(1)	3194(1)	3198(<0.5)	3195(2)	3189(1)	
3158(2)	3161(3)	3162(1)	3166(1)	3161(3)	3164(2)	3101(w) 3084(m)
3072sh(40)						
3064(63)	3068(78)	3065(86)	3068(65)	3076(76)	3067(64)	3063(m)
3045(42)	3056(52)sh			3065(56)sh	3058(42)sh	3056(sh)
	3038(10)	3038(1)		3043(11)	3036(8)	3032(m)
3023(9)	3023(8)	3024(1)		3026(7)	3023(7)	3021(m)
3001(3)	3004(4)	3004(1)	3007(2)	3003(6)	3004(4)	3002(m)
2971(3)	2971(4)	2973(2)	2986(2)	2978(4)	2977(3)	
	2924(1)		2937(10)	2914(2)	2936(1)	
	2897(1)	2906(1)			2905(1)	
				2894(1)	2890(1)	
2786(<0.5)	2769(1)	2772(<0.5)	2792(<0.5)		2774(<0.5)	
2722(<0.5)						
2580(<0.5)	2576(1)	2569(1)	2585(1)	2568(1)	2570(<0.5)	
			2249(4)			
		2098(2)				$\nu_{as}(NNN)$
	1639(1)sh					
1598(16)	1595(16)	1599(18)	1602(18)	1601(15)	1609sh	1604(sh)
1583(7)	1584(10)sh	1585(3)	1586(3)	1589(8)sh	1598(11) 1585(8)	1595(ms) 1582(sh)
		1490(1)	1499(<0.5)	1495(1)		1490(vs)
1445(1)	1448(1)	1450(2)	1450(2)	1447(1)	1449(1)	1448(vs)
		1380(1)	1377(<0.5)			1445(vs)
	1321(1)	1326(1)	1345(1)	1338(1)	1328(1)	1393(m)
1302(<0.5)	1303(<0.5)		1300(<0.5)			1325(ms)
	1284(1)	1282(1)		1283(<0.5)	1294(5)	1292(vs)
		1263(3)				1283(vs)
1217(3)	1213(4)			1219(2)		$\nu_s(NNN)$
	1203(4)					
1186(13)	1187(11)	1188(8)	1199(7)	1193(10)	1189(10)	1194(s)
						1188(s)
						1180(s)
1163(10)	1159(10)	1167(3)	1173(12)		1164(5)	1161(m)
1159(11)	1149(23)	1157(12)		1152(13)	1152(7)	1150(m)
					1123(23)	1124(vs)
1094(1)	1084(1)	1087(1)	1087(2)	1082(1)	1085(2)	1083(s)
1078(1)						
1057(2)					1065(1)	
1029(17)	1034(20)	1033(19)	1039(18)	1036(17)	1034(17)	1037(ms)
						1033(ms)
1004(65)	1003(54)	1002(68)	1005(66)	1004(35)	1003(40)	1002(ms)
	988sh			991(15)	995sh	991(w)
						985(w)
				965(3)	975(1)	976(w)

$(C_6H_5)CNH_2$	$(C_6H_5)CCl$	$(C_6H_5)CN_3$	$(C_6H_5)COH$	$(C_6H_5)CNF_2$	$(C_6H_5)CNSO$ Raman	IR
954(1)				952(3)	945(2)	942(w)
920(1)	932(1)	949(2)	927(3)	927(2)	936(3)	933(w)
910(1)	896(3)	900(3)		914(2)	906(2)	904(s)
					898(4)	898(vs)
867(2)			877(3)	881(1)		
849(1)	849(2)	844(1)		858(4)	861(<0.5)	
				848(3)sh		850(m)
		820(5)				847(m)
767(2)	766(1)	762(1)	766(2)	771(1)	755(2)	763(vs)
754(1)	741(1)	741(1)		748(<0.5)		758(vs)
				711(4)		747(vs)
700(14)	703(1)	704(3)	701(12)	703(5)	689(10)	703(vs)
	669(12)	670(4)		660(3)	653(2)	687(s)
					640(2)	652(s)
629(3)	629(3)					639(vs)
620(9)	619(6)	619(7)	621(9)	620(7)	621(7)	618(m)
585(1)				596(3)		
				541(5)	585(2)	582(m) $\delta(NSO)$
533(2)		531(1)			533(2)	531(m)
	511(1)sh	508(1)		517(1)	509(1)	502(s)
	497(7)					
445(2)		455(2)	450(1)		416(2)	416(s)
416(<0.5)	406(1)	411(4)				413(s)
						412(s)
376(1)		386(<0.5)	384(2)		389(3)	
342(1)	350(23)	334(2)	354(<0.5)	362(4)		
311(3)	319(6)	316(1)	319(<0.5)	312(8)	324(2)	
		307(1)			304(2)	
281(8)	281(13)	280(9)	285(9)	286(12)	281(9)	
250(9)	245(5)		249(7)	263(10)	253(3)	
234(2)		238(9)		239(3)	243(2)	
208(4)	183(13)	214(5)		188(2)	209(9)	
				140(15)sh	160(8)	
				129(27)sh		
111(90)				117(35)sh	116sh	
99(100)	102(100)	103(100)	94(100)	95(100)	105(100)	

w = weak; m = medium; ms = medium strong; s = strong; vs = very strong; sh = shoulder. <sup>a</sup> All data from this study.

**Table 2**  
 $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{14}\text{N}$  NMR Spectroscopic Data for  $(\text{C}_6\text{H}_5)_3\text{CNSO}$  in  $\text{CH}_2\text{Cl}_2$ .

		$\delta$ (ppm)	$\Delta\nu_{1/2}$ (Hz)
$^1\text{H}$		6.75 (m)	
$^{13}\text{C}$	o/m $(\text{C}_6\text{H}_5)_3$	128.19/128.62	
	p $(\text{C}_6\text{H}_5)_3$	127.64	
	ipso $(\text{C}_6\text{H}_5)_3$	144.50	
	$\text{C}(\text{C}_6\text{H}_5)_3$	80.98	
$^{14}\text{N}$		-39	700

Table 3  
Crystal Data for  $(C_6H_5)_3CNSO$ .

chemical formula	$C_{19} H_{15} N S O$
fw	305.38
T, K	223(2)K
space group	triclinic $P\bar{1}$ (No. 2)
$a$ , Å	8.9642(9)
$b$ , Å	9.2135(9)
$c$ , Å	11.0645(11)
$\alpha$ , deg	93.578(2)
$\beta$ , deg	101.098(2)
$\gamma$ , deg	118.142(2)
$V$ , Å <sup>3</sup>	778.24(13)
Z	2
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.303
$\mu$ , mm <sup>-1</sup>	0.209
$R_I$ , <sup>a</sup> $wR_2$ , [I > 2σ(I)]	$R_I = 0.0345$ , $wR_2 = 0.0910$
$R_I$ , <sup>a</sup> $wR_2$ (all data)	$R_I = 0.0409$ , $wR_2 = 0.0962$

<sup>a</sup>  $R_I = (\Sigma(F_O - F_C)/F_O)$ . <sup>b</sup>  $wR_2 = [\Sigma(w(F_O - F_C)^2)w/F_O^2]^{1/2}$ .

Table 4

Atomic Coordinates ( $x \times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $(\text{C}_6\text{H}_5)_3\text{CNSO}$ .

	x	y	z	$U(\text{eq})^a$
O(1)	2025(2)	5053(2)	5284(1)	51(1)
S(1)	601(1)	3352(1)	4857(1)	35(1)
N(1)	83(2)	2101(2)	5706(1)	29(1)
C(1)	678(2)	2061(2)	7047(1)	24(1)
C(2)	1161(2)	3684(2)	7898(1)	26(1)
C(3)	132(2)	4433(2)	7655(2)	33(1)
C(4)	501(3)	5854(2)	8438(2)	43(1)
C(5)	1899(3)	6541(2)	9483(2)	45(1)
C(6)	2910(3)	5794(2)	9747(2)	44(1)
C(7)	2548(2)	4370(2)	8960(2)	34(1)
C(8)	-884(2)	573(2)	7349(1)	25(1)
C(9)	-1029(2)	490(2)	8571(2)	32(1)
C(10)	-2418(2)	-865(2)	8844(2)	41(1)
C(11)	-3677(3)	-2151(2)	7898(2)	46(1)
C(12)	-3543(2)	-2081(2)	6683(2)	46(1)
C(13)	-2158(2)	-734(2)	6406(2)	35(1)
C(14)	2246(2)	1761(2)	7130(1)	25(1)
C(15)	3739(2)	2953(2)	6824(2)	31(1)
C(16)	5132(2)	2689(2)	6826(2)	39(1)
C(17)	5072(2)	1239(2)	7143(2)	43(1)
C(18)	3622(2)	68(3)	7469(2)	45(1)
C(19)	2210(2)	322(2)	7463(2)	34(1)

<sup>a</sup>  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor

Table 5

Experimental Bond Lengths [ $\text{\AA}$ ] and Angles [°] for  $(\text{C}_6\text{H}_5)_3\text{CNSO}$ .

O(1)-S(1)	1.450(1)	O(1)-S(1)-N(1)	122.61(8)
S(1)-N(1)	1.492(1)	C(1)-N(1)-S(1)	136.8(1)
N(1)-C(1)	1.486(2)	N(1)-C(1)-C(2)	111.8(1)
C(1)-C(2)	1.538(2)	N(1)-C(1)-C(8)	105.5(1)
C(1)-C(8)	1.542(2)	N(1)-C(1)-C(14)	105.3(1)
C(1)-C(14)	1.544(2)	C(2)-C(1)-C(8)	109.7(1)
C(4)-C(5)	1.382(3)	C(2)-C(1)-C(14)	112.5(1)
C(11)-C(12)	1.375(2)	C(8)-C(1)-C(14)	111.8(1)
C(16)-C(17)	1.382(2)	C(5)-C(4)-C(3)	120.2(2)

## **Figure Captions**

Fig. 1. Infrared and Raman Spectra of  $(C_6H_5)_3CNSO$ .

Fig. 2. Structure of the  $(C_6H_5)_3CNSO$  Molecule showing the Dimer Formation via S···O Contacts. Thermal Ellipsoids are shown at the 50% Probability Level.

Figure 1

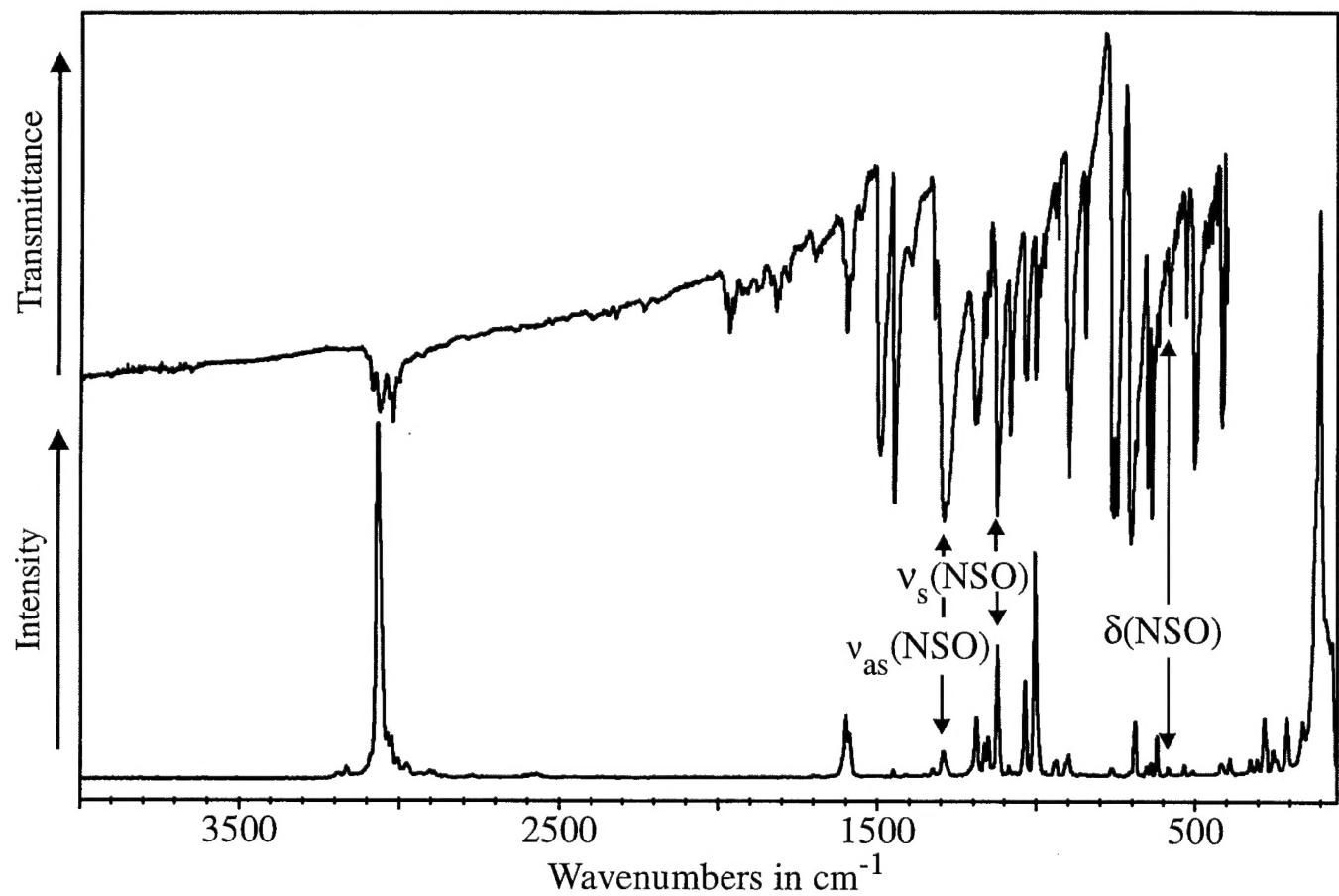
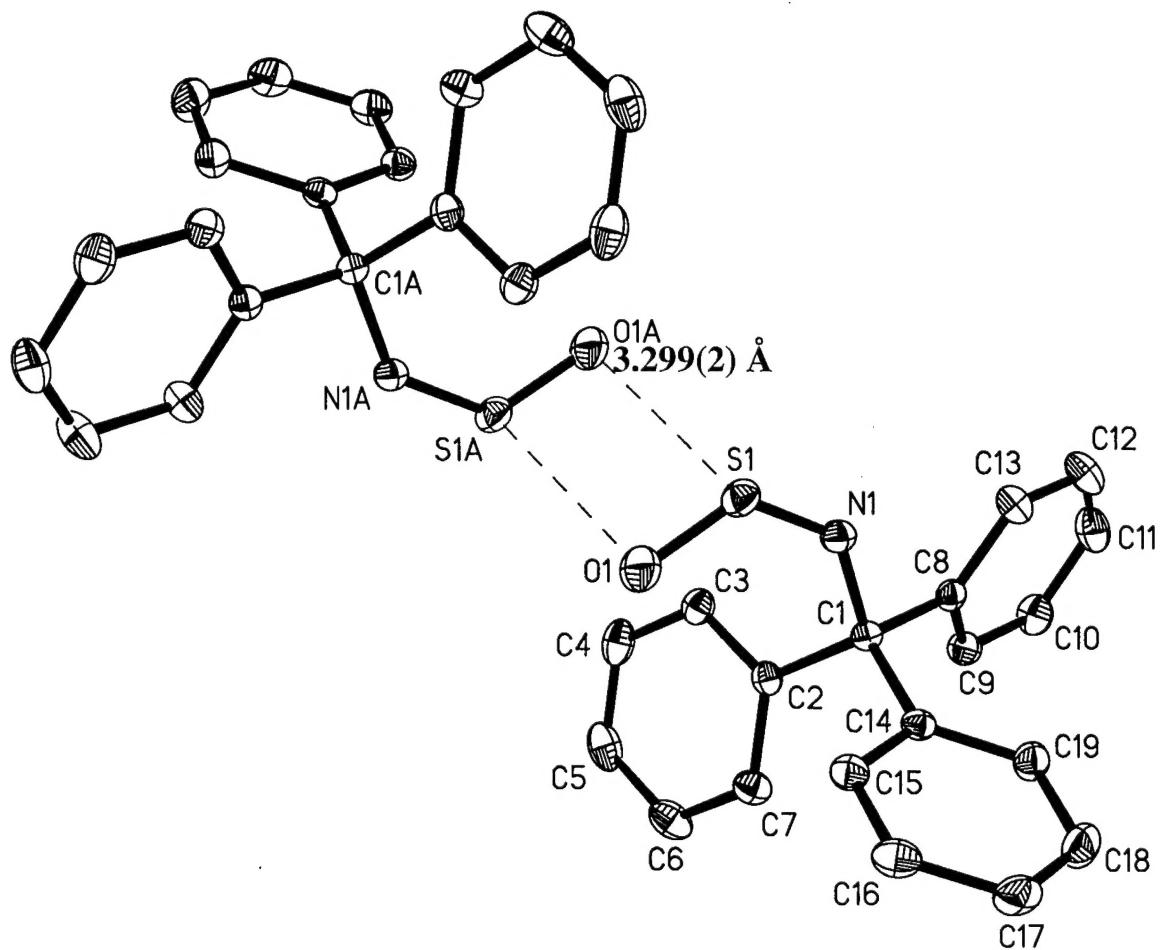


Figure 2



## Tritylsulfinylamine: A New Member in the Family of Sulfinylamines

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